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(54) 【発明の名称】 磁化可能なデバイス

(57) 【要約】

その上に磁化可能な層を含む磁気記録媒体であって、前記磁化可能な相が複数のフェリ磁性又は強磁性粒子を含み、各粒子の最大粒径が100nmより大きくなく、各粒子が分離した強磁性ドメインを有する前記磁気記録媒体を提示する。

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**Magnetizable device** This invention relates to the magnetizable device containing the magnetic layer which carried out domain separation and which consists of ferromagnetic particles of a nano-scale (for example, 1-100nm). The device which can magnetize this invention can be used as a magnetic storage device which improved the data storage property. Especially this invention relates to the magnetic storage medium containing a uniform ferromagnetic nano-scale (for example, 1-100nm) particle which carried out domain separation in the single domain which can be arranged to the usual 2D pack array useful to informational storage.

A magnetic medium uses a nano-scale (1-100nm) particle among paths with the possibility to super-high density ( $\geq 1$  Gbit/in<sup>2</sup>). More than the standard demand to a magnetic medium, there should be standard deviation of the particle size of a survivability granular medium small, and exchange decoupling (exchange decoupled) of the particle should be carried out. These demands are required to avoid a harmful medium noise. The current manufacture approach of nano-scale particles, such as arc discharge or multiple target ion beam sputtering, had not fully solved these two demands. Furthermore, when arranging to the array where the homogeneity particle was aligned, each particle can express informational "bit" in the location where making the effectiveness of a medium increase further is expected. This invention explains the manufacture approach of the granular medium which fills these demands for super-high density record in full detail. This invention is an open system which enables manufacture of the various magnetic adjusters which can carry out the stroke of the medium to various applications again.

Especially, this invention explains use of the ferritin which is iron storage protein which manufactures a nano-scale particle using the internal hole in full detail. Ferritin is used in iron metabolism in the everywhere in a living body kind, and the structure is saved in the living body kind at altitude. Ferritin consists of a subunit of 24 arranged so that hollow shell with a diameter of about 8nm may be offered. A hole usually saves 4500 iron (III) atoms which are the gestalten of a paramagnetism ferry hide light. However, this ferry FAIDO light can be removed (ferritin without a ferry hide light (ferrihydrite) is called "APOFERICHIZO"), and can make other ingredients incorporate. For example, it is raised to a ceramic, superparamagnetism magnetite, acetaminophen, and sweeteners Aspartame. In order to solve the problem of a magnetic medium, this invention contains the ingredient aligned in ferromagnetism.

By the first viewpoint of this invention, the magnetizable device containing the magnetic layer which the domain separated and by which the maximum grain size of each particle is constituted from a ferromagnetic particle which is not larger than 100nm is offered.

By the second viewpoint of this invention, it is a magnetic-recording medium containing a layer

magnetizable on it, and the layer in which said magnetization is possible offers said magnetic-recording medium containing two or more ferromagnetic particles showing the ferromagnetic domain which each particle separated more greatly [ the maximum grain size of each particle ] than 100nm. As for a magnetizable layer, being supported on a non-MAG substrate is desirable. By the third viewpoint of this invention, each particle has combined with the organic macromolecule (macromolecule), and the magnetic constituent containing two or more ferromagnetic particles whose maximum grain size of each ferromagnetic particle is not larger than 100nm is offered. As for an organic giant molecule, in this viewpoint of this invention, it is desirable that it is the ferritin which removed the usual core ferritin and was permuted by the ferromagnetic particle.

In this specification, the vocabulary "ferromagnetism" contains both of the ingredients, "ferromagnetism" and "ferrimagnetism." Usually in the field of electric engineering, it is used such.

The ferromagnetic particle used in this invention should have an ingredient and size which have a ferromagnetic property at a room temperature (for example, 15 degrees C - 30 degrees C). It is desirable, the maximum grain size of each ferromagnetic particle is large more more desirable than 50nm, and it is less than 25nm, and is most preferably smaller than 15nm. The maximum grain size of a ferromagnetic particle must not be as small as a particle loses the ferromagnetic property and becomes superparamagnetism in the operating temperature of a request of a record medium. Generally, in order to operate it at a room temperature, the maximum grain size of a magnetic particle means that it is not usually smaller than about 3nm. In the device which can magnetize the first viewpoint of this invention, and the magnetic preservation medium of the second viewpoint of this invention, in order to give the maximum number of the domain separated in the desired field and to provide a magnetic medium with the maximum storage capacity, the smallest possible one of the distance between adjoining ferromagnetic domains is desirable. Actual minimums differ on condition that others, such as temperature which uses various ingredients and magnetic media. However, an important demand is that an adjoining domain cannot interfere mutually magnetically, so that it can be changed by the domain where the magnetic alignment of the domain of arbitration adjoins. Generally, the minimum of domain spacing is about 2nm. The distance between adjoining domains is determined by the consistency of the separated domain which is demanded. However, since generally uses the possibility of the miniaturization offered by this invention, the distance between adjoining domains is not larger than 10nm.

Generally, the size of a particle is uniform. This means that the diameter at the maximum equator of a particle does not change rather than about 5%. One of the advantages which use the organic macromolecule combined with this magnetic particle in this invention is being able to choose the particle of a uniform particle size using this by surrounding a magnetic particle.

When a particle is a rotation ellipse-like (spheroidal), the diameter of a particle must not be larger than 100nm.

In the desirable mode of all the viewpoints of this invention, each ferromagnetic particle is wrapped in the organic macromolecule, or is wrapped partially. The vocabulary "a macromolecule" can mean the set of a molecule or a molecule, and, generally can have the molecular weight of less than 500 kDs to 1500kD. Ferritin has the molecular weight of 400kD(s).

a macromolecule wraps a magnetic particle -- or -- otherwise, it joins together by what (organize) is systematized, and; hole which can so contain the suitable hole which can contain a particle is

usually fully confined in the interior of a macromolecule. Moreover, although the macromolecule is not fully surrounded, it can contain reception and suitable opening (opening) which can be supported for a magnetic particle.;

For example, opening may be prescribed by the ring in a macromolecule. For example, the suitable giant molecule which can be used for this invention can raise protein (ferritin whose hole is empty), for example, protein apoferritin, a flagellum L-P ring, cyclodextrin, and the cyclic peptide that carried out self-organizing. Instead of wrapping a magnetic particle within a macromolecule, a magnetic particle may be systematized on S layers of macromolecules, for example, bacterial.

As other ingredients which can be used for systematizing a ferromagnetic particle in this invention, a system inorganic silica networks, such as an MCM type ingredient, DIN DORIMA, and micell type is raised.

A giant molecule desirable although it is used in this invention is apoferritin protein which has the hole of diameter the order of 8nm. The diameter of the ferrimagnetism which should be fitted within this protein, or a ferromagnetic particle should be 8nm or less.

It helps for the particle which this viewpoint of this invention which has coating combined to control condensation and oxidation, and for a domain to separate it.

As for a particle, in the device which can magnetize the first viewpoint of this invention, and the magnetic preservation medium of the second viewpoint of this invention, it is desirable to be arranged by the array of 2D order which obtains a super-high density magnetic medium.

Metal alloys, such as an alloy with which a ferromagnetic ingredient contains metal; aluminum, such as cobalt, iron, or nickel, barium, a bismuth, a cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, a praseodymium, samarium, strontium, titanium, vanadium, an ytterbium, yttriums, or those mixture; it may be metal ferrites [ , such as a ferrite ]; or the organic ferromagnetism ingredient containing barium, cobalt, or strontium.

When manufacturing a nano-scale particle, one of the main interests is that the particle manufactured is not superparamagnetism. Although a superparamagnetism particle has the permanent MAG hyperbolic child moment, the orientation of the moment about a crystallographic axis is changed by time amount. This is not useful for an actual magnetic storage medium. It depends for superparamagnetism on the volume, the temperature, and the anisotropy of a particle. The equation about these amounts can be guided through the problem of energy. The volume from which a particle becomes superparamagnetism (\*\*\*\*) is obtained by formula:\*\*\*\*= $25 \text{ kT/K}$  (k is a Boltzmann's constant among a formula, T is the Kelvin temperature of a particle, and K is the anisotropy constant of an ingredient). If this formula is used, the temperature ("blocking-proof temperature") from which a volume particle becomes superparamagnetism can be determined about an ingredient predetermined to the fixed volume. In a specific case, the fixed volume is 8nm in ferritin. When the cobalt metal particles which have only a crystal anisotropy (the value is  $45 \times 10^5$ ) are the balls which are the diameter of 8nm, blocking-proof temperature is 353 degrees K. This is in the temperature requirement experienced within a hard disk drive, and can prove that a cobalt particle is a useful storage medium. Clearly, there are other problems, such as coercive force of an ingredient, the moment, saturation magnetism, and the relaxation time. In spite of it, these are solvable by carrying out the stroke of the ingredient built into ferritin.

Ferritin is used in iron metabolism in the everywhere in a living body kind, and the structure is saved [ in the living body ] at altitude. Ferritin consists of a subunit of 24 arranged with the

symmetry of 432 which offers hollow shell with a diameter of about 8nm. A hole usually saves 4500 iron (III) of the gestalt of a paramagnetism ferry hide light. However, this ferry hide light can be removed (ferritin without a ferry hide light is called apoferritin), and can make other ingredients incorporate. the hole in 3 times and a 4 times shaft although the subunit of ferritin is wrapped strongly -- a channel exists in inside. If a channel is arranged in a line 3 times, the residual section combined with metals, such as cadmium, zinc, and calcium, exists. By incorporating such bivalence ion, it can promote it being potentially combinable with a ferritin molecule together, or they adjoining and arranging at least.

One of the approaches which manufactures the array in which the particle which has a uniform particle size to 8nm, and which was aligned in ferromagnetism carried out 2D pack By removing a ferry hide light core from ferritin natural in the inside of a water solution, and HOU-ized hydrogen sodium reduction of Co (II) water solution The cobalt metal particles aligned in ferromagnetism are included in a ferritin hole, It includes moving and carrying out the carbon coat of narrowing particle size distribution by ultra-centrifugal separation, pouring a particle into MES / compatible-under glucose liquid (subphase solution) with which 2D arrays gather on it, and the 2D array to a base. In this approach, the source of ferritin may be manufactured by a vertebrate, an invertebrate, vegetation, the bacillus, yeast, bacteria, or the recombination technique.

In an above-mentioned approach, a metal alloy core can be manufactured by HOU-ized hydrogen sodium reduction of a water-soluble metal salt. Other oxidization approaches contain carbon, a carbon monoxide, hydrogen, or a hydrazine hydrate solution. Moreover, a suitable solution can be oxidized and a metal ferrite core can be obtained. Oxidation is chemical or electrochemical and can obtain a metal ferrite.

In this approach, other approaches of choosing short or narrow particle size distribution, such as the long column meniscus exhausting method (short or longcolumn meniscus depletion methods) or magnetic field separation, can be used.

Furthermore, in this approach, cadmium, calcium, or the divalent metal salt containing zinc can be added in bottom compatible liquid, and particle adjustment can be promoted.

Furthermore, in this approach, the solution evaporation to a solid-state substrate top etc. can use other methods of arranging a particle to 2D array.

or [ furthermore, / having hydrogenated 2D array in this approach ] -- or carbon base films, such as carbon for diamonds which carried out the nitrogen dope, -- or a coat can be carried out with silicon base films, such as a silicon dioxide.

In this invention, the maximum grain size can shut up a ferromagnetic particle using the ferritin limited by the bore of 8nm of ferritin. A particle is manufactured by removing a ferry hide light core first and obtaining apoferritin. This is performed under a nitrogen flow by the dialysis to the sodium acetate solution which carried out buffer processing. A ferry hide light core is removed using the reducibility chelation which uses thioglycolic acid. Then, the ferry hide light which repeated the dialysis to a sodium chloride solution and was returned is completely removed from a solution. Once apoferritin is manufactured, ferrimagnetism or a ferromagnetic particle will be incorporated as follows. First, metal salting in liquid is returned under apoferritin existence. This is performed in an inactive environment and protects metal particles from the oxidation which lessens a magnetic benefit. The mixture of metal salting in liquid can be returned and an alloy or an alloy precursor can also be manufactured. All over a magnetic field, it is required for manufacturing a useful magnetic alloy sintering or to carry out annealing, and it obtains. An option is oxidizing the mixture of iron(II) salt and another metal salt. Thereby, the metal ferrite

particle which does not receive a bad influence from oxidation is obtained. As a useful metal salt, the salt of ammonium, barium, a bismuth, a cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, a praseodymium, samarium, strontium, titanium, vanadium, an ytterbium, and an yttrium is raised.

Narrow particle size distribution is required to avoid a medium noise. Although such distribution is acquired by various approaches including density gradient centrifugation or magnetic field separation, it is not limited to these approaches.

Although the manufacture approach explained in full detail uses natural horse \*\*\*\* ferritin, it should not be understood as this invention being limited to the source. Ferritin can be found out to what is manufactured by a vertebrate, an invertebrate, vegetation, the bacillus, yeast, bacteria, or the recombination technique. By manufacturing the variant apoferritin lacking in a bivalence joint site showed that variant protein countered roppo dense restoration of normal, and other things gathered to a slanting assembly.

While it is thought manufacturing a nano-scale particle that ferritin is an ideal system, it is not the only system which can use it. For example, a flagellum L-P ring is tubular protein with a bore of 13nm. By manufacturing 2D array of these protein, a metal film can be put on a tubular core and the perpendicular rod of a magnetic adjuster can be manufactured. The metal reduction under existence of a micro emulsion can also be used, and the nano-scale particle which carried out the coat with the surfactant can be manufactured. This invention is opened to other nano-scale particle manufacturing methods.

Finally, an array where the particle was aligned is desired. One of the approaches which performs this is because the water solution of a particle is poured into MES / compatible-under glucose liquid contained in a Teflon trough. In respect of the bottom phase boundaries of air -, breadth part denaturalizes and a particle forms a monomolecular-layer film. 2D array of the wrapped particle takes place under this monomolecular layer. A substrate is moved for an array and a monomolecular layer by interpositio Lycium chinense on a direct monomolecular layer after 10 minutes at a room temperature for 5 minutes at a substrate. After collecting substrates, the coat of the array which adhered is carried out with the carbon thin film for protection. 2D array is acquired by other approaches, such as solution evaporation to a solid-state substrate top, again, and it should not be understood as this invention being limited to the array approach.

Example 1 This example explains manufacture of the apoferritin from horse spleen ferritin concretely. From a calcium free-lancer's natural horse \*\*\*\* ferritin (CalBiochem and 100mg/(ml)), to the sodium acetate solution (0.2M) processed by the buffer by pH5.5 under the nitrogen flow according to the reducibility chelation which uses thioglycolic acid (0.3M), apoferritin removed the ferry hide light core by dialysis (the molecular weight of 10-14k dalton is removed), and was manufactured. The reducibility ferry hide light core was completely removed from the solution by repeating dialysis to a sodium chloride solution (0.15M).

Example 2 This example explains manufacture of a cobalt metal concretely within apoferritin. Apoprotein was added in deaerated TES / sodium chloride solution (0.1/0.4M) which was processed by the buffer by pH7.5, and the used solution of about 1mg [ /ml ] protein was obtained. It was made for all the atomic numbers that added gradually the deaerated cobalt (II) (as acetate) solution (1mg/(ml)), and were added to serve as about 500 atoms / apoprotein molecule. This was stirred in the inert atmosphere at the room temperature for one day. Then, the cobalt (II) salt was returned with hoe-ized hydrogen sodium, and it considered as the cobalt (0) metal. The product finally obtained was a cobalt particle solution with which each particle is surrounded by ferritin shell.

Example 3 This example explains concretely manufacture of metal alloys, such as yttrium cobalt (YCo5), within apoferritin. The metal alloy was obtained by using the ratio of 1:5 of yttrium (III) opposite cobalt (II) (as acetate) (as acetate), although it was the same approach as an example 2. The product finally obtained was an yttrium cobalt particle solution with which each particle is surrounded by ferritin shell.

Example 4 This example explains concretely manufacture of metal ferrites, such as a cobalt ferrite ( $\text{CoO-Fe}_2\text{O}_3$ ), within apoferritin. Apoferritin was added in deaerated MES / sodium chloride solution (0.1/0.4M) which was processed by the buffer by pH6, and the used solution of about 1mg [ /ml ] protein was obtained. It added gradually and air oxidation of the 1:2 deaerated solutions of cobalt (II) (as acetate) and iron (II) (as for example, an ammonium-sulfate salt) was carried out. The product finally obtained was a cobalt ferrite particle solution with which each particle is surrounded by ferritin shell.

Example 5 This example explains concretely 2D array of the magnetic particle wrapped in ferritin. The water solution (it is the thing of examples 2-4, and the homogeneity of the particle size is chosen) of a particle was poured into MES / compatible-under glucose liquid (0.01M / 2%) contained in a Teflon trough. Breadth part denaturalized to the bottom phase-boundaries side of air -, and the particle formed the monomolecular-layer film in it. 2D array of the wrapped particle took place under this monomolecular layer. The array and the monomolecular layer were moved for the substrate by interpositio Lycium chinense on the direct monomolecular layer after 10 minutes at the room temperature for 5 minutes at the substrate. After collecting substrates, the coat of the array which adhered was carried out with the carbon thin film for protection.

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CLAIMS

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[Claim(s)]

1. Ferromagnetic particle which carried out domain separation and whose maximum grain size of each particle is not larger than 100nm Magnetizable device containing the magnetic layer constituted.
2. It is a magnetic-recording medium containing a layer magnetizable on it, and the layer in which said magnetization is possible Ferromagnetic DOMEI which each particle more nearly roughly [ the maximum grain size of each particle ] than 100nm separated Said magnetic-recording medium containing two or more ferromagnetic particles showing N.
3. \*\* according to claim 2 whose distance between adjoining ferromagnetic domains is at least 2nm Mind record medium.
4. Claim 2 whose distance is not larger than 10nm or three publications between adjoining ferromagnetic domains Magnetic-recording medium.
5. Any 1 term publication of claims 1-4 by which each ferromagnetic particle is wrapped in organic macromolecule Magnetic-recording medium.
6. Claim by which each ferromagnetic particle is wrapped in hole of protein macromolecule, or opening circles Magnetic-recording medium given in five.
7. Each ferrimagnetism or a ferromagnetic particle is wrapped in apoferritin protein. Magnetic-recording medium according to claim 6.
8. Each particle has combined with the organic macromolecule and the maximum grain size of each ferromagnetic particle is 100nm. Magnetic constituent containing two or more ferromagnetic particles which are not large.

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